



Short Communication

**Investigating the Effect of Fullerene on the Basicity of Paraphenylenediamine
by using the Quantum Chemistry Methods**

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ABSTRACT

In this study, paraphenylenediamine was first bonded to the fullerene and was optimized geometrically by Using the quantum chemistry methods. paraphenylenediamine was examined in the isolated state and in the fullerene-bonded state via carbon atoms. In the theoretical research, the simulation was done by the Gauss View software. Then, the bonding orbital calculation was done by using the NBO method. All the calculations were performed by the Hartree-Fock method in the 6-31G* (HF/6-31G*) level of theory and the Gauss View and Gaussian 2003 software in the gas phase. The contribution of p-orbital in the N-H bond, the natural charge and the number of valence electrons on the nitrogen atom at the site bonding to the fullerene were investigated in the isolated state and in the fullerene-bonded state. All evidence showed a decrease in the basicity of the nitrogen atom at the site of bonding to the fullerene.

Keywords: Fullerene, the participation of p-orbital, NBO, Hartree-Fock

Introduction

Today there are more than 30 types of fullerene, most notably C₆₀. The fullerene consists of 20 hexagonal and twelve pentagonal rings as the basis of an icosohedral symmetry closed cage structure. In 1996, Harold et al. won the Nobel Prize for discovering the fullerenes. [1-10]

Since fullerenes do not have a chemical group available for substitution reactions, they only engage addition reactions. Fullerene derivatives are used as enzyme inhibitors. Fullerenes have shown that they are capable of counteracting a few types of cancer cells. [11-23]

Due to their hollow spherical structure, they are used as medication carriers. Essential enzymes, hormones or medications can be attached to the inside or outside of the fullerenes; thus, they have many uses in Nano-medicine. [24-27]

Paraphenylenediamine (PPD) is a synthetic chemical compound widely used in synthetic hair colors. It is also used in the rubber and print industries. This compound is colorless, light pink, gray or yellow and in the form of solid crystals, and typically becomes red, brown, and finally black when it is exposed to the air and oxidized. The user has to be cautious and prevent this chemical compound having direct contact with his/her skin. Recent studies have reported that the risk of cancer increases in people who have been exposed to this substance for long. [28-30]

The compound produced by bonding paraphenylenediamine to the fullerene (C₆₀-PPD) (figure. 1) act as the inhibitor of Carbonic anhydrase XII (one of the Carbonic anhydrase enzymes released in tumor cells in response to the oxygen deficiency) through interaction with the active part of the enzyme [31-35].

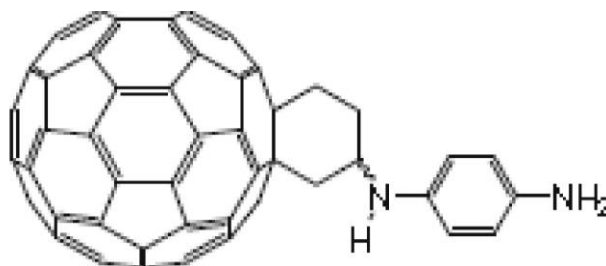


Figure 1. C₆₀-Paraphenylenediamine

2. Computational Methods

For the present study, all the calculations about C₆₀-paraphenylenediamine compound were done by using the Gauss View and Gaussian 2003 software in the gas phase. The compounds were first optimized by using the Hartree-Fock method in the basis set 6-31G* (HF/6-31G*). Then, the NBO calculations were done. The p-orbital participation and the length of the nitrogen bond at the site bonding to the fullerene were investigated in two states (figure 2), in the isolated state and in fullerene-bonded state. The results can be found the following tables and diagrams.

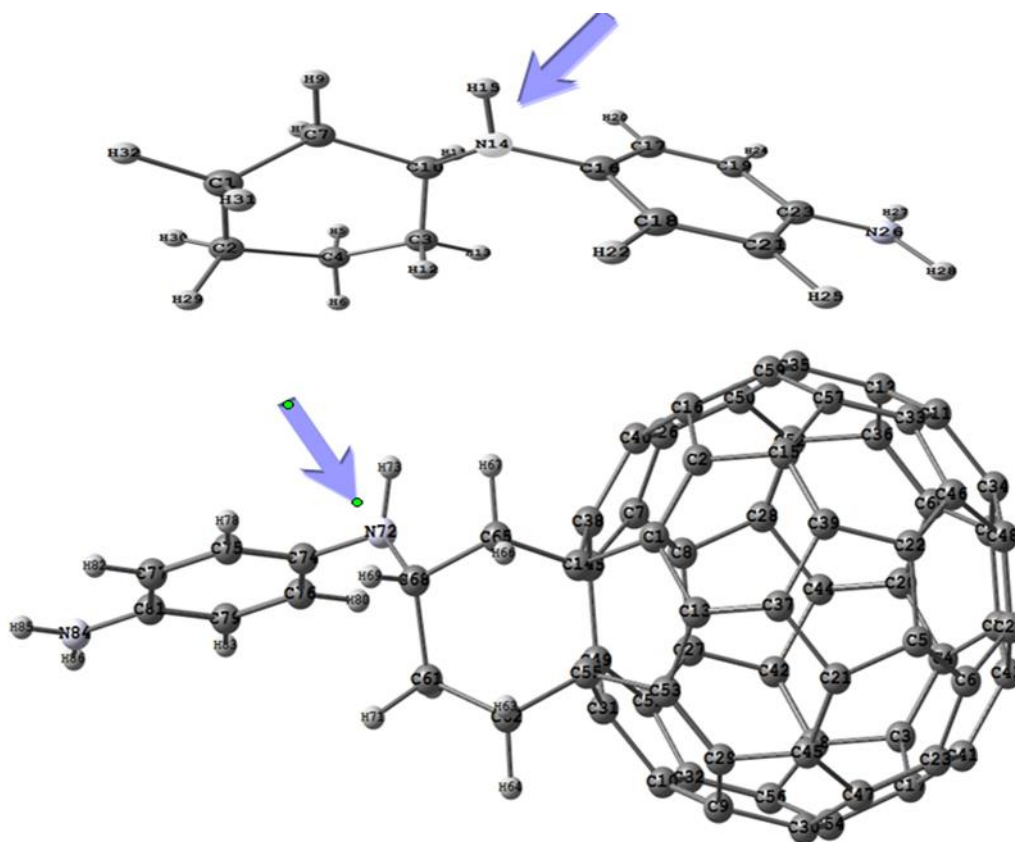


Figure 2. Paraphenylenediamine, the fullerene, and the examined sites

Table 1. The participation of the p-orbital in the examined states

P-orbital Participation	Sigma Bond	
2.97581	$BD(\sigma)_{N14-H15}=0.8379(s^1p^{2.90})+0.5459$	PPD- N14-H15
2.918736	$BD(\sigma)_{N72-H73}=0.8392(s^1p^{2.83})+0.5438$	C60-PPD- N72-H73

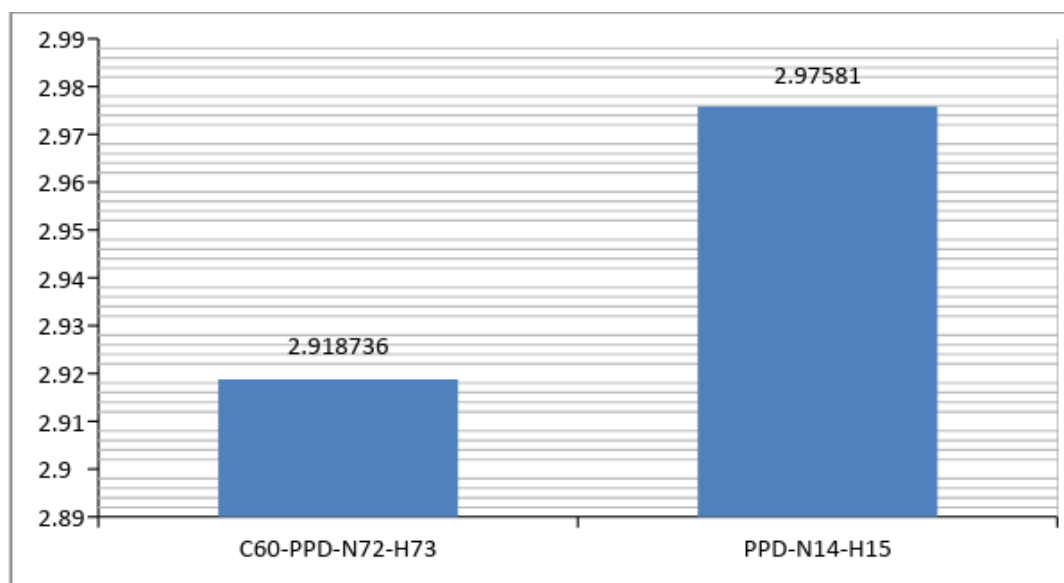
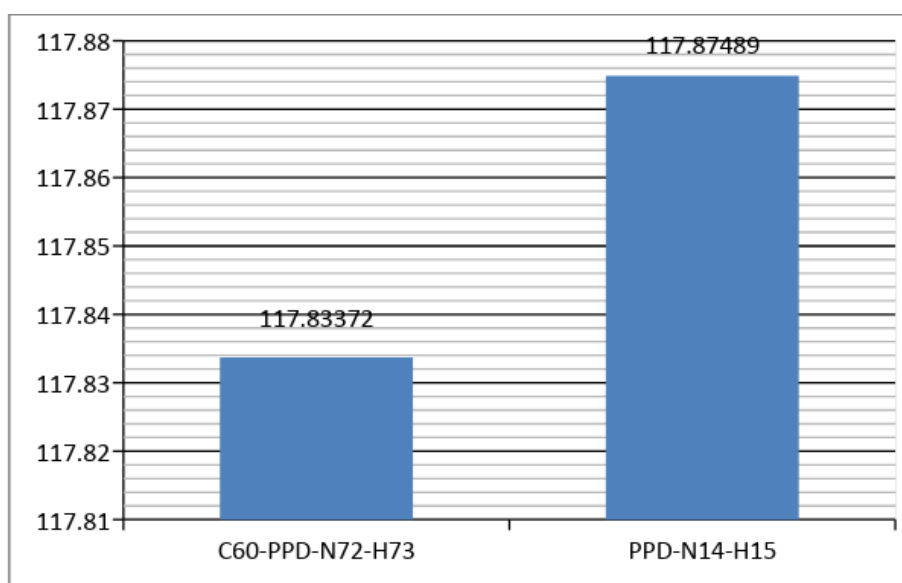
**Figure 3.** Comparing P-orbital participation in two states: PPD & C₆₀-PPD

Table 2. Comparing the nitrogen bond lengths in two states: PPD & C₆₀-PPD

Bond Lengths		
PPD	N14-H15	117.87489
C ₆₀ -PPD	N72-H73	117.83372

**Figure 4.** Comparing the bond lengths in two states: PPD & C₆₀-PPD**Table 3.** The amount of the natural charge on the nitrogen atom

PPD	- 0.76447
C ₆₀ -PPD	- 0.76253

Table 4. The number of the valence electrons on the nitrogen atom

PPD	5.75061
C ₆₀ -PPD	5.74863

3. Conclusion

Since the p-orbital is more expanded than the s-orbital, an increase in the participation of the p-orbital leads to an increase in the bond length. According to the tables 1-4 and the diagrams 1 and 2, bonding PPD to the fullerene nano-carrier led to a decrease in the participation of the p-orbital and the bond length in the examined states.

Considering the decrease in the participation of the p-orbital and the increase in the participation of the s-orbital, it can be concluded that the base property of the nitrogen atom decreases at the site bonding to the fullerene.

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